USE OF EQUIMOLAR CYSTEINE/ASCORBIC ACIDS TO RECOVER MCP SYNTHESIZED Ti(Mg) alloy

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Abstract

Dissolution of waste by-products of mechanochemical processing (MCP) synthesis of Ti(Mg) alloy, from TiO_2 and 15 wt.% excess Mg, was conducted in equimolar cysteine/ascorbic acids. The synthesized alloy is inherently mixed with MgO and other oxides of Ti and the objective was to leach out the by-products of the MCP process and hence recover a pure isolated Ti-Mg powder.

The dissolution of particulate polycrystalline MgO and TiO_2, and Ti-20Mg solid solution (obtained from milling blended elemental powders) was also investigated to note how they individually behaved in the leach reagent. The study indicated that separation was possible although with considerable contamination from MgO and TiO_2 and inadvertent co-dissolution of Ti(Mg) alloy. Further work on sequential dissolution of the by-products using equimolar cysteine/ascorbic acids and inorganic acids is recommended. Equimolar cysteine/ascorbic acid leach reagent was effective in dissolving TiO_2; while inorganic acids will dissolve MgO. It is envisaged that sequential dissolution will minimise the unintended co-dissolution of the Ti(Mg) alloy.

Introduction

Ti(Mg) alloy powder has been produced by mechanochemical processing (MCP) of TiO_2 with 15wt.% more than stoichiometric Mg. MCP is a novel, 'far from equilibrium' solid-state process for the manufacture of metal powders, including metal alloy powders by ambient temperature reduction of a reducible metal compound by a reactive metal [1].   The process, however, also produces MgO, unreacted TiO_2, Mg and type TiO_{1-x} oxides [2]. It is required that the Ti(Mg) alloy powder be isolated from the by-products of the process by a possible hydrometallurgical process, where the by-products are leached out while the Ti(Mg) alloy is preserved and recovered.

Organic acids ascorbic acid/cysteine acid in equi-molar concentrations [3] were used in the leaching experiments to recover the synthesized Ti(Mg) alloy powder. The use of the test leaching media will be counter-balanced by the need not to dissolve the Ti(Mg) alloy formed during the MCP process.

Experimental Procedures

The TiO_2-Mg powder was made by mixing 80g TiO_2 with 56g Mg (the amount of Mg added represented the sum of the stoichiometric mass and 15wt.% excess). Stoichiometric quantities of TiO_2 and Mg powders were mixed on the basis of Eq. 1. Still from Eq. 1, and assuming total reduction of the TiO_2, the maximum theoretical amount of free Ti formed was calculated. It was on the basis of this amount of Ti that can be theoretically formed that the mass of 15wt.% excess Mg was calculated. The

sum of the excess Mg (Eq. 2) and the stoichiometric TiO_2 and Mg (Eq. 1) formed the precursor powder blends for MCP.

$$TiO_2 + 2Mg \Rightarrow Ti + 2MgO \qquad\qquad \text{(Eq. 1)}$$
$$Ti + 15wt.\%Mg \Rightarrow Ti(Mg) \qquad\qquad \text{(Eq. 2)}$$

The TiO_2-Mg powder sample used for the hydrometallurgical separation project was continuously milled for 32 hours, with a ball: powder ratio of 20:1 and at a mill speed of 800 rpm. The alloy Ti-20Mg was formed from milling the respective blended elemental powders under the same conditions as the TiO_2-Mg blends. The powders were characterized for phase and particle size distribution.

Mechanochemically processed TiO_2-Mg (including unprocessed TiO_2-Mg, Ti and Mg) were taken for phase analysis by XRD, using X'Pert Pro MPD, Philips PW1710 diffractometer, to determine the phases present and, henceforth, ascertain the relative degree to which the reduction and alloying had progressed. Leached powder residues were also taken for XRD analysis to determine the phases that resisted dissolution, and their relative intensities. Analysis of the residue phases should, therefore, give an indication of those phases that would have largely dissolved in the individual leach reagents.

The morphology of both pre-milled and milled samples was investigated using a Jeol JSM-6300F scanning electron microscope (SEM) at an accelerating voltage of 15 kV. The samples were coated with carbon to enhance conductivity, and hence achieve better resolution of the micrographs. The morphology of the unmilled and MCP TiO_2-Mg help to explain the progress of reduction and/or alloying; composition becomes homogenous and there will be no distinction between the initial powders [4].

The separation of the waste constituents (by-products TiO, MgO; and incompletely reduced oxides of Ti and Mg) from the Ti-Mg alloy powder was done through direct dissolution in equi-molar cysteine/ascorbic acids [3]. The organic reagent cited above give a good dissolution of TiO_2, a difficult to dissolve phase, potentially present from aerially re-oxidised Ti. The dissolution experiments were carried out in a Julabo SW23 Shaking Waterbath, equipped with a removable shaking carriage for accommodating the individual 250ml dissolution flasks. For each run, an acid solution of pre-determined molarity in the range 0.025 – 0.8M was charged into a flask and heated 60°C. Thereafter, a powder sample (liquid/solid ratio of 100ml/1g) was added to the flask and the contents stirred at a constant speed of 200 rpm. The flasks openings were sealed with aluminium foil to minimize spillage of contents and evaporation of the leaching reagents during the agitated, heated leach runs. The waterbath setup was placed in a fume cupboard. Blended elemental Ti-20(wt.%)Mg milled powder, and polycrystalline TiO_2 and MgO were also subjected to the leaching reagent above to determine their individual behaviour and subsequently extrapolate it on the dissolution of the MCP synthesized powders. The TiO_2 and MgO were not pre-milled.

Results and Discussion
## XRD characterisation of powders

Figure 1 show the XRD patterns of MCP processed TiO_2-Mg powder mix as well as the unprocessed TiO_2-Mg, Ti-20Mg alloy powder and elemental Ti and Mg. The peaks of incompletely reduced TiO_2 are visible as well as the peaks for the products of the MCP which are Ti-Mg alloy and MgO. The patterns also show the strength (hence the relative abundance of each constituent) of the peak intensities relative to each other. MgO and the Ti-Mg alloy are the major phases and they occur at seemingly overlapping 2θ values of 36.5, 42,5 and 62°.
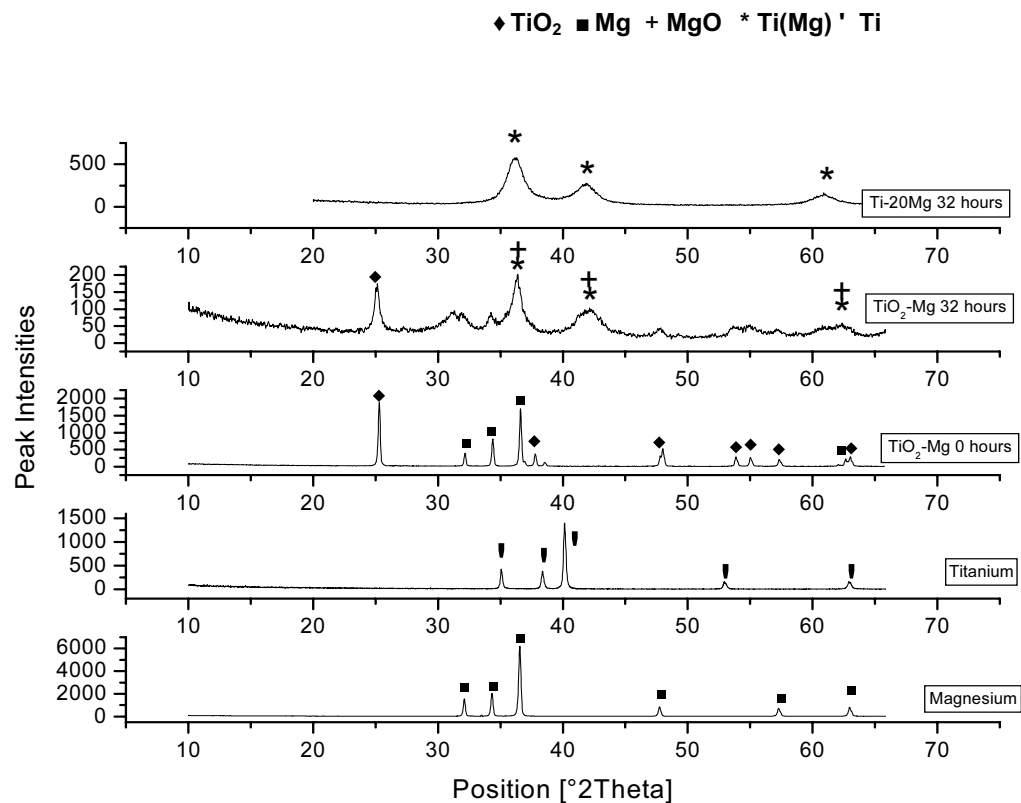
Figure 1: XRD patterns of mechanochemically processed (as well as unprocessed) TiO_2-Mg, Ti-20Mg alloy and elemental powders

On MCP processed TiO_2-Mg, the MgO and Ti(Mg) overlapping peaks are seen to be more intense than any other peak, with TiO_2 peaks being the second most prominent peaks on the pattern. The overlapping phases of MgO and Ti-Mg had broader, less intense peaks indicating that their crystallinity was low. It has been shown that while 2 wt.% of a material can be detected if the particle size range is 26 -38 microns, 25wt.% is required if the particle size range is 0.05 – 1 microns (Shankar et al, 2003). MgO is synthesized from simple reduction of the oxide, while Ti(Mg) is formed as a direct result of mechanochemical processing, where steady state sizes are achieved due to the balance between fracturing and rewelding typical of milling operations. This causes a

narrowing of the size range [6]. A direct result of this would be that Ti(Mg) alloy powder was on the smaller side of the size range, making MgO the more dominant phase on the overlapping phases on XRD (Figure 2).
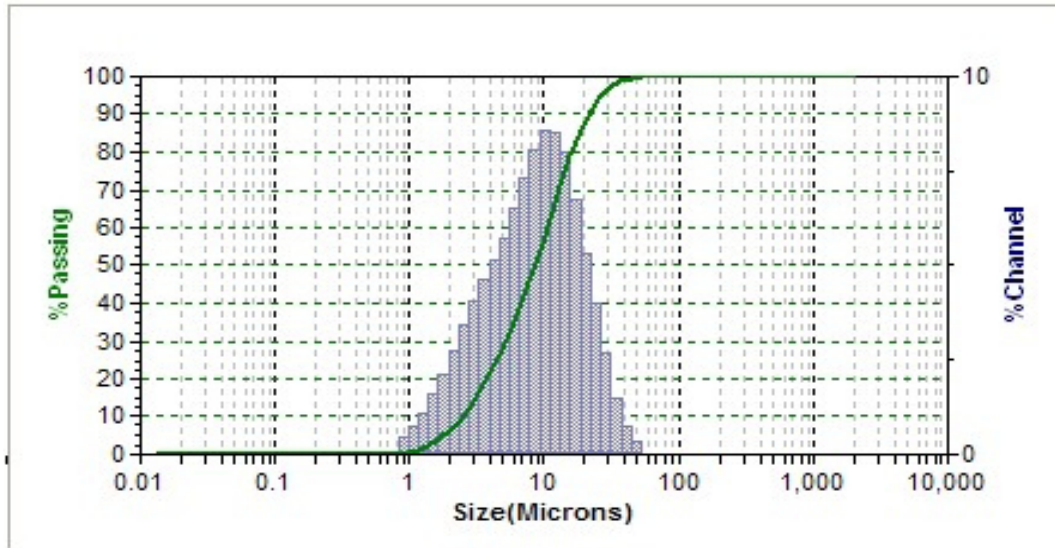
Figure 2: Particle size distribution of TiO$_2$-Mg powder milled for 32 hours

The extent of the reduction of TiO$_2$ by Mg was evaluated from the Eq. 3 [4]:

$$D = (\frac{I(TiO_2)}{[I(TiO_2) + I(MgO)]}) \times 100 \qquad \text{(Eq. 3)}$$

where I is the intensity of the diffraction peaks of MgO and TiO$_2$. The reduction of TiO$_2$ was evaluated from Eq. 3 to be 90%. The assumption in using Eq. 3 was that there was no formation of substoichiometric oxides of Ti; that is there was complete reduction to give elemental Ti for any given TiO$_2$ molecule or there was no reduction at all. Thus, 10% of the TiO$_2$ remained unreduced at the end of the milling process and the rest took part in the mechanochemically induced reduction and alloying.

The expected products (MgO and Ti-Mg) and their masses, assuming the reaction goes to completion, are 81g MgO and 55g Ti(Mg) alloy. All the excess Mg was expected to go into solution with Ti to form the Ti-Mg alloy powder. However, this was not entirely the case as the XRD pattern of the MCP powders showed evidence of oxides of Ti. The reduction reaction did not go to completion.

Of the 80g TiO$_2$ added, 72g (90%) was reduced by the reductant Mg. From this, and using proportion calculations, it was found that the masses of products at 90% reduction were 73g MgO and 43g Ti. The amount of Mg in the MgO product is 44g; thus the difference of 12g (from the 56g initially added) went towards mechanical alloying with free Ti from the reduction process. The amount of free Ti at 90% TiO$_2$ reduction was

calculated to be 43g such that the total mass of Ti(Mg) alloy synthesized was 55g. This translated to weight percentages of 6% TiO_2, 54%MgO and 41% Ti(Mg). Thus 41% Ti(Mg) alloy powder was synthesized from the MCP process.

Morphological evolution of MCP powders

| (a) TiO₂ | (b) Mg | (c) MCP TiO₂-Mg |
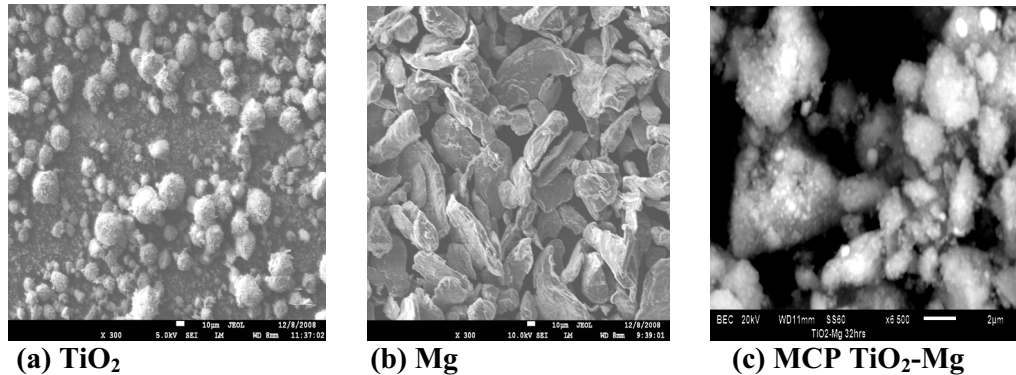
Figure 3: SEM micrographs of the starting powders and the mechanochemically processed TiO₂-Mg

The Mg (flaky) and the TiO_2 (round) powder particles lost their initial morphologies which were replaced by a globular morphology; the TiO_2 powder particles were indistinguishable from the Mg (Figure 3). TiO_2 particles, which are expected to be brittle, already fractured and were lodging themselves into the soft Mg particles [6]. Higher magnifications revealed that the globular particles themselves were agglomerates of smaller particles that appeared to be welded together. This evolution of morphology is in line with the ball milling process which proceeds through repeated welding, fracturing and rewelding of powder particles [6].

Dissolution experiments for the different powder phases
Dissolution experiments were done on processed TiO_2-Mg (and its unprocessed equivalent) as well as on Ti-20Mg alloy and commercial MgO powders. A leach reagent of ratio 100ml/1g was used; ratio was deliberately made high and is ideal, from the viewpoint of fundamental kinetic analysis, to decrease the viscosity and consequently the mass transfer resistance in the acid-powder particle interfaces [7]. Lower ratios are only more realistic from an industrial and scale up point of view. Further, the acid will be sufficient to react evenly with each and every constituent in a given powder without affecting the dissolution or lack thereof of the other constituents.

### Effect of leaching in equi-molar cysteine/ascorbic acids
Figure 4 shows the dissolution of the different powder samples in equi-molar cysteine/ascorbic acids. The dissolution of TiO_2 and Ti-20Mg showed a sharp increase on moving from a concentration of 0.025M to 0.05M. 32% TiO_2 and 42% Ti-20Mg dissolved at 0.05M acid. Beyond 0.05M there was a drastic increase in the masses of TiO_2 and Ti-20Mg residues. The TiO_2 gradually dissolved with increase in the equimolar concentration until about 29% residue was left at 0.8M. On the other hand, Ti-20Mg began to show marked resistance to dissolution beyond 0.05M with the

residue proportion gradually picking up with increase in the equimolar concentration until it was about 75% at 0.8M.
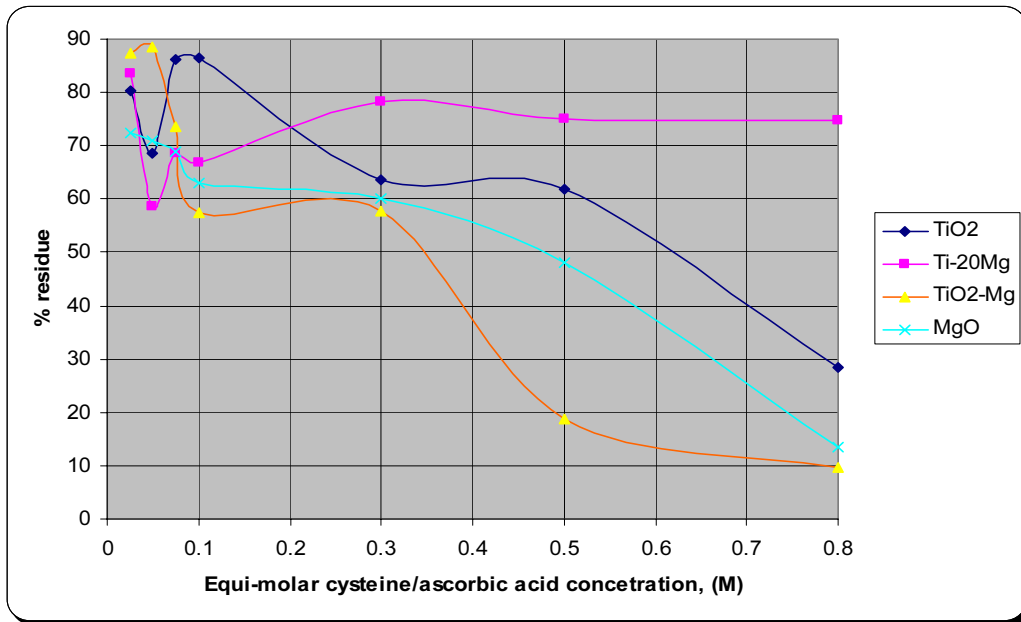
Figure 4: Effect of equimolar cysteine/ascorbic acids on the leaching of the individual powders

Meanwhile, MCP TiO$_2$-Mg and MgO showed gradual decrease of their residue proportions with increase in the equimolar concentration. Mechanochemically processed TiO$_2$-Mg, from which 51% MgO and 6% incompletely reduced TiO$_2$ (total 57%) need to be leached out, was drastically dissolved until only 9% residue remained. MgO steadily dissolved until 13% MgO residue remained after leaching in 0.8M cysteine/ascorbic acids.

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♦ **TiO₂** ▪ **Mg** + **MgO** * **Ti-Mg**
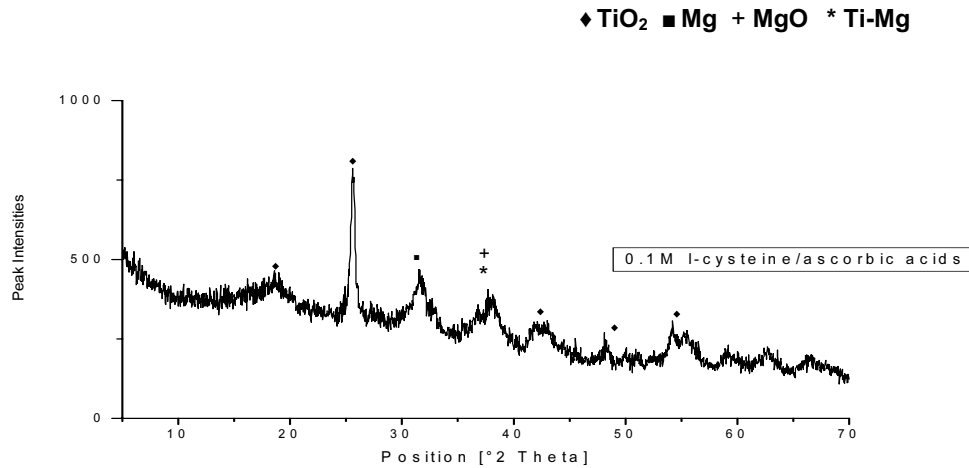
Figure 5: XRD pattern of milled TiO₂-Mg residue leached in 0.1M equimolar cysteine/ascorbic acids

Figure 5 shows the XRD spectra of the mechanochemically processed TiO₂-Mg powder mixture leached in 0.1M cysteine/ascorbic acids. The peaks of incompletely reduced oxides of Ti are visible although and are the most dominant. The XRD pattern corroborated the results from leaching (Figure 4) which showed that TiO₂ was resistant to dissolution. The MCP TiO₂-Mg residue decreased from 88% to 10% and this went way below the theoretically calculated Ti-Mg proportion of 41%; most of the value Ti-Mg was lost to inadvertent co-dissolution. Meanwhile, independent polycrystalline MgO was not completely dissolved. This can be confirmed by the presence of MgO peaks in the XRD patterns.

Conclusions
From the study carried out on recovery of MCP synthesized Ti(Mg) alloy powder using equimolar cysteine/ascorbic acids organic it was concluded that recovery of the Ti(Mg) powder was achieved by leaching with organic acids. This was, however, with contamination from TiO₂ which did not completely dissolve.
Future work will investigate on cyclic leaching, as well as sequential dissolution, with different leach reagents. Different reagents attack the powders differently, some more (or less) drastically than others. So it could be possible to select a variety of leach reagent combinations and durations which will leave the pure Ti(Mg) alloy while maximizing dissolution of the waste powders.

References
[1] McCormick, P.G., Tsuzuki, T., Robinson J.S., Ding J. (2001) Nanopowders synthesized by mechanochemical processing, Journal of Advanced Materials, 1008-1010.

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[2] Koch., The synthesis and structure of nanocrystalline materials produced by mechanical attrition, Nanostructured materials Volume 2. (1993), pp. 109–129.

[3] Mukherjee A, Raichur A. M, Modak J. M; Dissolution studies on TiO_2 with organics, ScienceDirect Hydrometallurgy, 2005, pp585 - 588.

[4] Lai M.O, Lu L and Chung B.Y; Formation of Mg-Al-Ti/MgO composite via reduction of TiO_2, Composite Structures 57 pp 183-187, 2002.

[5] Shankar V., Lu L., and Lai M.O; Mechanochemical activation of solid state reaction between Mg and TiO_2, JSME International Journal, Series A, Vol. 46, No.3, 2003, pp 251 – 254.

[6] McCormick P.G and Froes F.H, The fundamentals of Mechanochemical Processing JOM 50, 1998, pp 61.

[7] Sasikumar C., Rao D.S., Srikanth S., Mukhopadhyay N.K. and Mehrotra S.P; Dissolution studies of mechanically activated Manavalakurichi ilmenite with HCl and H_2SO_4, Scince Direct, Hydrometallurgy 88 (2007) 154–169.

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